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Grau de Química

Treball Final de Grau

Development of PSkits for fast and selective analysis of ^{99}Tc.
Desenvolupament de PSkits per l'anàlisi selectiu i ràpid de ^{99}Tc.

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January 2021

UNIVERSITAT DE BARCELONA

B:KC Barcelona Knowledge Campus
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Nothing in life is to be feared, it is only to be understood.

Now is the time to understand more, so that we may fear less.

Marie Curie

Agradecer a Àlex Tarancón, José F. García y resto del equipo QUESTRAM R toda la atención y ayuda ofrecidos durante la realización de este trabajo. Gracias por hacerme sentir como en casa.

A mi familia por el apoyo incondicional y paciencia que han tenido conmigo. En especial a ti, papa, por ser mi referente y estar a mi lado siempre.

También a todos los amigos y amigas que me llevo después de estos últimos años, que son muchos. A Paula, por aparecer y animarme siempre que lo he necesitado.

Gracias. Gracias. Gracias.

REPORT

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1. SUMMARY

The dismantling of nuclear plants will experience an increase in the following years around Europe and it will require a great number of radioactive residues analysis that may imply significant economic cost. For this reason, the obtention of fast and selective identification methods for alpha and beta emitters in liquid samples is a topic of interest for the future.

The aim of this project has been to design a fast and selective method for characterization of beta radionuclides by using plastic scintillator foils that, with the addition of a selective extractant, generate what is known as PSkits. Specifically, the study has been focused on the detection of ^{99}Tc, an important residue from nuclear power plants.

The synthesis of porous foils of polystyrene with fluorescent solutes has been studied in a polymerization process. Different experimental conditions have been studied in order to ensure porosity and fastening of the foils to the scintillation vials where they are prepared. In addition, with the use of a selective extractant for technetium as a recovering, the selective PSkits applicable to liquid samples have been generated.

From the results, it has been seen that the purification of the monomers reduced the interference phenomenon in the scintillation process. In addition, the presence of DVB increased the rigidity of the foil and gave stability without modifying the scintillation capacity. Furthermore, heptane has been proved as an acceptable porogen and both plastic and glass scintillation vials presented selective retention capacities over 95%.

Detection efficiencies in glass vials were around 20%, whereas plastic vials were rounding 50-60%, being the last mentioned the ones with better results.

It can be concluded that the developed method, based on foils, has been satisfactory for the detection of beta emitters, although it will require an extensive optimization work to ensure robustness.

Keywords: Decommissioning, Beta emitters, Plastic scintillation, Technetium

2. RESUM

El desmantellament de plantes nuclears experimentarà un augment en els propers anys per tot Europa i seran necessaris un gran nombre d'anàlisis de residus radioactius que pot implicar un cost econòmic important. És per aquest motiu que l'obtenció d'un mètode d'identificació ràpid i econòmic d'emissors alfa i beta en mostres líquides és un tema d'interès pel futur.

L'objectiu d'aquest treball ha estat dissenyar un mètode de caracterització ràpid i selectiu per radionúclids beta per mitjà de làmines de centellejador plàstic que, recobertes d'un extractant selectiu, generen el que coneixem per PSkits. Concretament, l'estudi ha estat centrat en la detecció de ^{99}Tc, un residu important provinent de centrals nuclears.

S'ha portat a terme la síntesi de làmines poroses de poliestirè que presenten soluts fluorescents encapsulats mitjançant un procés de polimerització. S'han avaluat diverses condicions experimentals per assegurar la formació de porus i que les làmines quedin fixades als vials de centelleig on es preparen. A més, amb l'ajut d'un extractant selectiu per tecneci utilitzat com a recobriment, s'han generat els PSkits selectius aplicables a mostres líquides.

Dels resultats s'ha vist que la purificació dels monòmers redueix els fenòmens d'interferència en el procés de centelleig. S'ha comprovat que la presència de DVB incrementa la rigidesa de la làmina i atorga estabilitat sense afectar a la capacitat de centelleig. A més, s'ha vist que l'heptà funciona adequadament com a porogen i que, tant els vials de centelleig de plàstic com els de vidre, presenten capacitats de retencions selectives superiors al 95%.

Les eficiències de detecció en vials de vidre han estat al voltant del 20% mentre que els de plàstic ronden el 50-60%, sent aquests darrers els que semblen obtenir millor resultats.

Es pot concloure que el mètode desenvolupat basat en làmines ha donat resultats satisfactoris per detecció d'emissors beta, tot i que requerirà d'un extens treball d'optimització per assegurar la seva robustesa.

Paraules clau: Desmantellament, Emissor beta, Centelleig plàstic, Tecneci

3. INTRODUCTION

3.1. RADIOACTIVITY

3.1.1. Radioactive emission

A radioactivity process occurs when there is a spontaneous transformation of an unstable atom into another by the emission of energy in form of nuclear particles and electromagnetic radiation. Radioactive emissions can be classified in three different categories:

- Alpha particles (α)

The disintegration process for alpha particles consists in the emission of a helium nuclide, which is formed by two neutrons and two protons. It is common for radioisotopes with high atomic weights (A>150) and it is doubtful for lighter atoms [1].

Due to the fact that the particles of helium present a considerable mass compared to other particle emissions and they are charged, alpha particles present the lowest penetration power (lower than 50 μm in water) because they can interact easily with molecules in the medium. They can be stopped by a paper foil.

The disintegration process is represented in the next equation:

$$ {}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}He $$

- Beta particles (β)

A beta particle is an electron (negative charge) or positron (positive charge) that is emitted from the nucleus of an unstable atom when a neutron becomes a proton and vice versa. The disintegration process for each one is represented by the following expressions.

1) When a neutron becomes a proton and emits electron and antineutrino:

$$ {}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + e^{-} + \bar{\nu} $$

2) When a proton becomes a neutron and emits positron and neutrino:

$$ {}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y' + e^{+} + \nu $$

The positron and the electron have a very low mass compared to helium particles (α) and they present a higher penetration power (from μm to cm). They can be stopped by an aluminium foil, 1,5 mm of Pb or laboratory glassware. This process is common for almost every atom regardless the atomic number (Z), even though the most usual beta emitters present high number of neutrons in their nucleus.

- Gamma radiation (γ)

When an alpha or beta decay is produced the nucleus may be still excited, and it can emit gamma radiation in order to reach the ground state. So, the majority of alpha and beta emissions are accompanied by gamma radiation. The main difference between alpha, beta and gamma emissions is that gamma rays are electromagnetic radiation of high energy that can penetrate into matter, human skin and even some thin Pb walls.

The next equation shows the gamma emission process:

$$ {}^{A}_{Z}X^{*} \rightarrow {}^{A}_{Z}X + \gamma $$

3.2. DECOMMISSIONING OF NUCLEAR POWER PLANTS

It is estimated that over the next years, a huge number of nuclear power plants all over the world will be undergoing decommissioning process. The dismantling of these facilities will require the analysis of large number of samples in different mediums to determine the specific radioactive nuclides present in them. In order to accomplish that, a substantial investment will be needed if there is no improvement in the waste characterization, conditioning, storage and disposal. International organizations like OECD Nuclear Energy Agency (NEA) have already called about the needs in R+D innovation for decommissioning of nuclear facilities [2].

One of the most common features of all decommissioning processes is the characterisation and survey of waste, which is present at different stages of any project. Developing the means that allow us to identify and quantify contaminants (in solid or liquid samples) in real-time, with minimum invasion and being usable *in*-situ, would result in a more complete cost-effective characterisation.

The main difficulties reside in the correct identification of the hazardous radiological and non-radiological contaminants without exposure of the technicians. Some of these species are relatively easy to identify, as gamma emitting radionuclides, while others like pure alpha and beta emitters involve off-site analysis in the laboratories. This is due to the difficulties in their detection

caused by interferences of matrix components and spectrometric interferences from other radionuclides that require from previous chemical separation.

3.2.1. Technetium (^{99}Tc)

^{99}Tc is a pure beta emitter (E_{max} = 291 keV) produced usually during thermal fission process of ^{235}U and ^{239}Pu in nuclear power plants (NPP), where its concentration as a waste is significant. This isotope is a long-lived radionuclide ($T_{1/2}$ = 2.13x10^5 years), which presents high mobility in solid/water systems in TcO_4^- form and can diffuse with ease into the environment [3][4].

Due to its high mobility, high fission yield, and long half-live, ^{99}Tc is one of the most important radionuclides to keep track of in decommissioning of NPPs, management of nuclear waste and in environment control [5][6].

3.3. RADIOACTIVITY DETECTION

There are different efficient techniques to measure radioactivity, but the most common methods to determine beta emitters are ICP-MS and scintillation techniques.

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique used to measure long-lived radionuclides even at environmental levels. It is able to quantify almost all beta or alpha emitters, although it can result in a time-consuming technique with large times of analysis in the laboratories due to the separation procedures needed to remove interferences. In order to accelerate the waste characterization process it might be better to look for a quicker and more economic on-site screening method in spite of being less sensitive. A rapid screening can provide useful information on the presence or not of contamination by radioisotopes in NPPs decommissioning materials [7].

Scintillation counting techniques, liquid scintillation (LS) and plastic scintillation (PS), are consolidated and robust methods for the measurement of alpha and beta emitters in liquid samples and, moreover, they can be adapted for fast screening analysis

3.3.1. Liquid Scintillation

Liquid scintillation (LS) technique has its origin with Reynolds experiments in late 40s and 50s when observing fluorescence produced by some organic solutions after being irradiated. The kinetic energy of the emitted beta particles was transformed into photons thanks to the organic

scintillators. These produced photons could be converted quickly, by means of a photomultiplier, into electronic pulses that could be detected.

Nowadays, liquid scintillators are understood as a mixture of an aromatic solvent like xylene, toluene or benzene, with fluorescent solutes like PPO and POPOP; and with some surfactants to be able to hold aqueous samples. The solution generated is called liquid scintillator cocktail (LSC) and it is added to the active sample solution which contains the radionuclide.

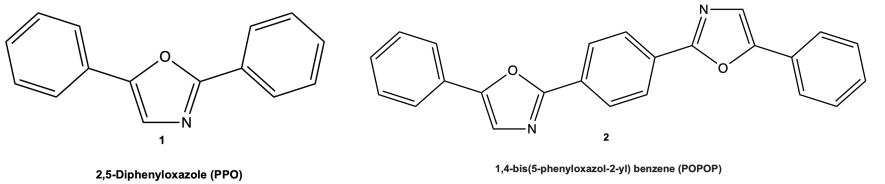

Figure 1. Solid reagents PPO and POPOP

When the radionuclide emits the beta particle, its energy is transmitted to the aromatic solvent molecules by ionization and excitation processes. Then, the energy is liberated from the solvent to the primary fluorescent solute, which is excited. The transfer of energy when returning to the ground state emits photons in UV region (350-400nm). To increase the wavelength of emission and increase the detector response, the additional secondary fluorescent solute (spectrum shifter) absorbs the light from the primary solute and reemits it with a larger λ, shifting the energy emitted to the visible electromagnetic spectrum (400-500 nm) and matching the maximum detection range of the photomultiplier (PMT).

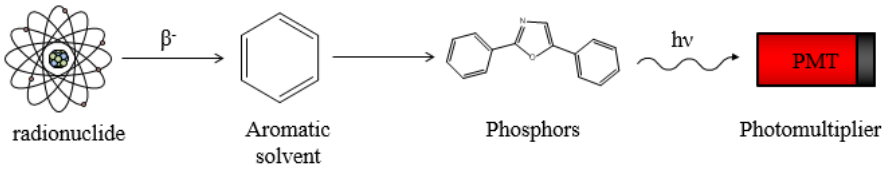

Figure 2. Diagram of LS mechanism

When the photons interact with the PMT, the electronic pulses are augmented thousands of times due to the high voltage applied. These pulses are registered by the counter in different channels depending on the energy of the pulse, which is proportional to the number of photons emitted in each flash. From the obtained values, the scintillation detector can find the count rate which is the number of counts per unit of time (counts per minute, CPM; or counts per second,

CPS) and it is able to generate a spectrum that gives information about the energy of the emitting radionuclides. In the case of technetium, which is a low beta emitter, the spectra should appear at low energies [1][8].

The detection efficiency is used to indicate the fraction of particles (α,β,γ) that reach the detector window and can be registered. In fact, it is a quality parameter of the scintillation process. It is calculated as a percentage relation between the net count rate detected by the counter and the disintegrations per unit of time of the radionuclide (DPM), which are equivalent to activity:

$$\text{Detection efficiceny} = \frac{\text{Net count rate (CPM)}}{\text{Activity (DPM)}} \text{x } 100 \qquad (1)$$

However, while working with scintillation techniques, it is important to consider the fact that when the energy transfers are produced, some of them may experiment processes that result in fewer counts detected by the counter. The reduction of intensity in the emission produced by a radionuclide in a sample is known as Quenching.

There are different types of quenching: particle (affecting the process on the path that follows the emitted particle before achieving the scintillator), ionizing (when there is a reduction in the excitation of the scintillation molecules), chemical (if there are interferences in the energy transmission between solvents and solutes), colour (when the medium presents colour and absorbs the emitted photons) and optical (when the change in the refraction index reduces the photons transmission). Although the best-known processes are ionization, colour and chemical quenching, all of them reduce the intensity of the emission produced, change the position of the spectrum to lower energies and reduce the efficiency of the detection system [9].

Some scintillation parameters actually help to quantify these effects, being the SQP(E) the one used in this work by a Quantulus scintillation counter. The SQP(E) corresponds to the endpoint channel which limits the 99.75% of the total counting from the spectrum generated by an external source, generally ^{152}Eu. This parameter can be used as a reference to see the possible shifts in the spectrum due to quenching or other effects [3].

Liquid scintillation technique (LS) is the most common method used for detection of alpha and beta emitters and it has been consolidated as a robust technique for the analysis of environmental samples. One of the advantages is that sample preparation is pretty simple and by just mixing the active solution with the LSC in a vial, the sample is ready to be measured. As LS is normally working with aqueous samples, some of the quenching effects (particle or optical) are reduced.

However, LS presents some limitations when working with strong salt matrixes due to the fact that a biphasic solution is generated and, in order to achieve homogeneity, laborious work in the lab is required. Another problem appears with the separation of alpha and beta particles because their signals are overlapped in the spectrum. Furthermore, beta emitters are not monoenergetic; which means they present continuous spectrum of energies that may be overlapped even with other beta radionuclides. Lastly, this technique tends to generate radioactive and organic mixed wastes that need to be treated with care due to its hazardous content [10].

Thus, even LS is a great technique with high detection efficiency values for alpha and beta radionuclides in aqueous samples, it presents complications when looking for ultra-fast selective screening applications, as we are doing in this work.

3.3.2. Plastic Scintillation

Plastic scintillation (PS) is an alternative to LS that has also been developed recently as an effective and selective technique for the measurement of alpha and betta emitters.

The composition of PS is equivalent to that of LS cocktails, but the scintillator includes a polymeric solvent, a crosslinker that transforms the polymer into a more resistant and rigid 3D-structure and the fluorescent solutes (PPO, POPOP, ...). Due to its plasticity, plastic scintillators can be obtained in a diversity of forms like microspheres (PSm) or foils (PSf) which open up new possibilities of working.

The mechanism of scintillation in PS is similar to the LS with the difference that the base materials are polymers with linear chains that follow a polymerization process in order to be generated. However, due to the intrinsic features of the PS compared to the LS, it might have higher distances between sample-scintillator and different quenching effects that reduce the detection efficiency.

One of the advantages of the heterogeneity that the solid scintillator presents is that, with the addition of other substances, the structure can be modified and adapted to the measure requirements. For instance, it is possible to add porogens like heptane or toluene that allow to increase the specific surface of the PS and even improve the efficiency of detection.

Furthermore, the addition of a selective extractant to the surface generates a PSresin (PSr) that grants selectivity for the radionuclide under the study. This is an important advantage in the analytical process due to the fact that if the selective porous PSf is directly generated inside the

vial, the separation work and the reagents needed are reduced considerably as well as the sample measurement becomes simpler. By just filling up the vial, mixing it and emptying the vial again, the measurement would be ready and fast results would be obtained.

Besides, the heterogeneous medium of the PS reduces the generation of organic wastes, avoiding liquid extractions and making this technique more economic, less toxic and all in one single support.

Although this may cause an important reduction in the detection efficiency, in this work we are looking for a fast-screening method that allows any technician on-field to easily identify and separate liquid samples containing technetium. For this, high detection efficiencies are not crucial and for all the above mentioned, a PS vial with selective resin for the radioisotope seems to be adequate for this study.

4. OBJECTIVES

The aim of this study was to develop a first prototype of PSkits as an economic, fast-selective technique for the screening analysis of ^{99}Tc in liquid samples.

To achieve that objective, this work would consist in:

- To synthesize stable and porous PSfs with optimization of reagents and conditions.
- To calibrate the PSfs for specific analysis of ^{99}Tc.
- To evaluate the application of PSkits in liquid samples containing ^{99}Tc.

5. EXPERIMENTAL SECTION

5.1. REAGENTS

All reagents used for the study were of analytical grade. 2,5-Diphenyloxazole (PPO), 1,4-Bis(5-phenyl-2-oxazolyl)benzene (POPOP) and 2,2'-Azobis(2-methyl-propionitril) (AIBN) were purchased from Acros Organics, Sigma-Aldrich and Fluka, respectively. Styrene (St), Divinylbenzene (DVB) and Aliquat 336® were purchased from Sigma-Aldrich. Ethanol (EtOH), toluene and n-heptane were supplied by VWR Chemicals. Hydrochloric acid fuming 37%(HCl), hydrofluoric acid (HF) and methanol (MeOH) were supplied by Merck. Alumina (aluminium oxide) and glass wool were purchased from Alfa Aesar and PanReac AppliChem. 20 mL glass and polyethylene scintillation vials and OptiPhase HiSafe 3 (used as LSC cocktail) were supplied by Perkin Elmer. The stock solution of ^{99}Tc (activity: 2,820 Bq/g) was supplied by Amersham.

5.2. INSTRUMENTS

AG245 and AT261 analytical balances from Mettler Toledo, automatic pipettes of different volumes from RANIN E4 XLS, P-Selecta oven, MS 3 digital Vortex mixer and Dry block heater 3, both from IKA®, were used for the synthesis. End-over-end mixer has been used for the polymer cleaning. Radioactive measurements have been done in a Wallac 1220 Quantulus Scintilaltion Spectrometer form Perkin Elmer with multichannel analyser. PSfs images were obtained with Jeol JSM-7001F FESEM in Facultat de Medicina de la Universitat de Barcelona.

5.3. SYNTHESIS OF PSFS

PSfs have been always synthesized following the polymerization technique. Table 1 shows the amount of reagents needed for the synthesis using 1 mL of styrene (St) or mixture of St and divinylbenzene (DVB).

Table 1. Plastic scintillator solid reagents regarding 1 mL monomer

Reagent	**Amount regarding monomer** [mg]
PPO	27.18
POPOP	0.45
AIBN	0.63

Styrene and DVB may have been purified before use depending on the conditions of the experiment. To perform the purification, they were filtered through aluminium oxide in a syringe with glass wool.

All the solutions were prepared by weighing and were left polymerizing for 20h at 70ºC in a dry block heater. When the process was finished, the PSfs were rinsed three times with ethanol to remove the porogen and monomers that had not reacted.

In order to establish the optimal procedure for the generation of the PSf samples, these were prepared in different conditions:

- 8:1 St:DVB proportion non-purified and with 0, 0.5 or 1 mL of toluene as porogen in glass vials
- 8:1 St:DVB proportion non-purified and with 0, 0.5 or 1 mL of toluene as porogen in glass vials previously attacked with HF
- Different series of St:DVB (1:0, 32:1, 16:1, 8:1, 4:1, 2:1) non-purified and without porogen in glass vials
- 1:0 and 2:1 St:DVB purified without porogen in glass vials
- 2:1 St:DVB proportion purified with 0, 0.5 or 1 mL of toluene as porogen in glass vial
- 2:1 St:DVB proportion purified with 0, 0.5 or 1 mL of heptane as porogen in glass vial
- 2:1 St:DVB proportion purified without porogen in plastic vials
- 32:1 St:DVB proportion purified with 1 mL of heptane in glass and plastic vials
- 2:1 St:DVB proportion purified with 1 mL of heptane in glass and plastic vials

5.4. PREPARATION OF PSKITS

For the preparation of the PSkits, 1.5 mL of the extractant solution (1.036 g Aliquat 336® in 100 mL of methanol) were poured over the surface of the PSfs in the vials and the methanol was left to be evaporated in the oven at 40-50ºC. In order to ensure a slim film of extractant without lumps, the evaporation was made with successive additions of a decreasing volume of solvent (0.5, 0.25 and 0.1 mL) to the PSfs once most of the extractant solution was evaporated. The slim surface of extractant was characterized by the SEM.

5.5. RADIOACTIVITY MEASUREMENT

5.5.1. PSfs sample preparation

25 µL of ^{99}Tc solution of 7 Bq/g (420 cpm) were dropped on surface of the PSf and the vials were placed in the oven at 40ºC, where they were left without caps for 2 hours, evaporating the solution and allowing the ^{99}Tc to spread progressively in the surface of the PSf. Once the technetium solution was evaporated, the vials were measured in the Quantulus scintillation counter.

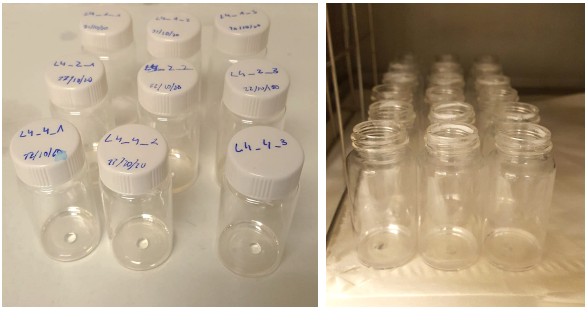

Figure 3. Drops of ^{99}Tc in PSfs

5.5.2. PSkits sample preparation

In order to determine the efficiency of detection and retention of the PSkits, 10 mL of 0.1M HCl solution and 0.3 mL of ^{99}Tc-D3 (activity: 44.37 Bq/g) stock solution were added together to the scintillation vials with soft manual agitation.

In order to know the detection efficiency of the ^{99}Tc retained on the PSKits, once the samples had been mixed, the 10 mL of solution were removed from the vial with automatic pipette and the PSkit was measured in the scintillation counter.

5 mL of the solution removed from the PSkit were added together with 15 mL of liquid scintillator cocktail (LSC) in a 20 mL plastic scintillation and were measured in the Quantulus scintillation counter after mixing in the Vortex for 3 minutes to ensure one homogeneous phase.

Below is shown the scheme of the procedure of the measurement of the PSkits (Figure 4).

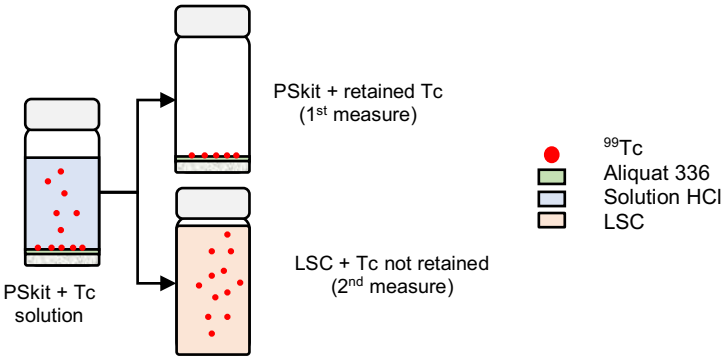

Figure 4. PSkits measurement procedure

5.5.3 Determination of the LS detection efficiency

In order to determine the LS detection efficiency: 5 mL of HCl solution, 0.1 mL of ^{99}Tc-D3 (activity: 44.37 Bq/g) and 15 mL of LS cocktail were added together in the respective plastic and glass vial, both without PSkits present. Once the measurement was made, the extracted value of efficiency for both plastic and glass vials, along with the count rate given by the counter allowed us to determine the efficiency of the LS.

5.5.4 Quantulus Counter configuration

The PSfs and PSkits samples were measured for an hour using the same protocol, which had been programmed to detect high energy beta emitters (^{14}C). This configuration offers an extended dynamic quench range and provides multi-parameter spectrum analysis to correct for luminescence, colour quenching and background radiation for beta particles. The coincidence bias (trigger threshold level) was set to low pulses in order to include all of them in the counting.

The parameter SQP(E) is calculated automatically by the detector by using an external gamma-ray source (^{152}Eu) and the counting time set for the measurement of the gamma-ray source was of 2 minutes.

5.6. DATA TREATMENT

All the data of this study has been treated with Microsoft office Excel and MATLAB R2020b software. A Savitzky-Golay function incorporated in MATLAB has been used to smooth the different spectra showed.

In order to calculate the efficiency of detection and the retention constant, the next expressions have been used:

- The detection efficiency of PSkits and LS measurement is expressed as the ratio between the net counts detected and the activity added to the vial.

$$\text{Detection efficiceny} = \frac{\text{Net count rate (CPM)}}{\text{Activity (DPM)}} \text{x } 100 \qquad (1)$$

- The retention constant corresponds to the remaining activity in the PSkit regarding the activity added to the vial. The retained activity of the sample can be obtained by subtracting the activity in the solution extracted from the PSkit (waste) from the activity of the sample retained.

$$\text{Retention constant} = \frac{\text{Activity of Sample} - \text{Activity of waste}}{\text{Activity of Sample}} \text{x } 100 \qquad (2)$$

The activity of the waste was calculated in plastic and glass vials as the ratio between the net count rate of the waste and the efficiency detection of the LS previously calculated.

$$\text{Activity of Waste} = \frac{\text{Net count rate of waste}}{\text{LS Efficiency}} \text{x } 100 \quad (3)$$

6. RESULTS AND DISCUSSION

The results obtained in this project are centred in two ambits. First, the synthesis of porous and stable PSfs and PSkits and secondly, the characterization of the capacity of detection and retention of ^{99}Tc by the PSkits.

6.1. SYNTHESIS OF PSFS

6.1.1. PSfs with 8:1 proportion

First series of PSf were prepared using a 8:1 St:DVB proportion in glass vials with increasing amounts of toluene as porogen: without toluene, with 0.5 mL and with 1 mL. PSf obtained are shown in Figure 5.

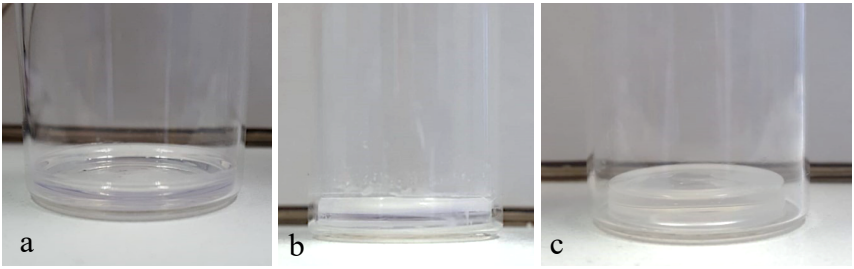

Figure 5. PSf formed without porogen (a) with 0.5 mL (b) with 1 mL (c)

The PSf prepared without toluene (a) presented uniform, transparent and colourless surface glued to the glass. For the PSf prepared with 0.5 mL of toluene (b), some of the foils presented deformations in the surface and were not properly glued to the glass. Moreover, there was a reduction in the volume of the PS foil. Finally, in the PS with 1 mL of toluene (c), almost all of the PSf had a significant reduced volume and were not glued to the glass vial.

It can be concluded that in these conditions stable porous PSfs cannot be obtained. It seems that the presence of toluene might not allow the polymer to be properly attached to the glass, and when ethanol rinsed the porogen, the polymer got limp and slippery, making some of the replicates to reduce their volume and to not be glued to the glass.

New PSf were prepared using the same proportion 8:1 but the conditions of the synthesis were changed. The aim was to see if modification of some parameters during the polymerization process could help to obtain more stable PSfs. The conditions studied were:

- Glass vials with etched surface: The glass scintillation vials were previously treated with a 10% HF solution for 24h before polymerization in order to etch the internal surface vial by the reaction of the silicates of the vial with the HF and help to immobilize the PSf. No success was obtained and the PSfs were not fixed to the vial.
- Pre-polymerized vials: It was thought that the possibilities to glue polymer to another polymer were higher than to fix them to the vial glass. Therefore, a double polymerization process was carried out; first, without the addition of toluene and later with the addition on 0.5 mL of toluene. It was observed that the polymerization solution of the second foil dissolved the previous PSf and it was impossible to obtain a stable double foil.

Figure 6. Double polymerization result

- 48 hours polymerization: The polymerization process was maintained during 48h in order to see if, with the increase of polymerization time, the PSf could get better linked to the glass vial but not success was obtained from this experiment.
- Fast drying at 70ºC: The evaporation of the non-reacted monomers took place inside the block heater at 70ºC instead of being done at ambient temperature as in the rest of the experiments. No success was achieved, and the foils continued to be not glued to the glass vial.

6.1.2. PSfs with variable St:DVB proportion

Once the evaluation of different conditions that affected the vial and the polymerization process tested unsuccessful to produce stable PSs, a new series were generated with different relations of St:DVB and without porogen addition. The objective was to see how the concentration

of DVB could affect the stability of the PSfs. DVB acts as a cross-linker giving rigidity and chemical resistance to the polymer.

The PSfs polymerized without crosslinker addition (1:0) were opaque while the ones with DVB were more transparent, as shown below.

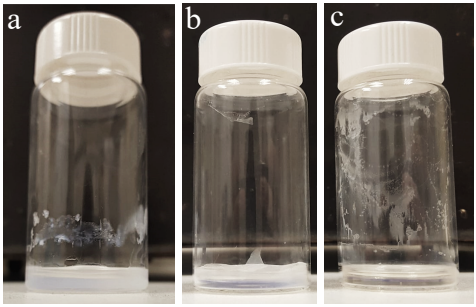

Figure 7. PSfs of different St:DVB proportions (a) 1:0 (b) 32:1 (c) 2:1

Furthermore, PSfs which had higher concentration of DVB (4:1 and 2:1) presented yellow colouration that might cause colour quenching in the measurement (Figure 8).

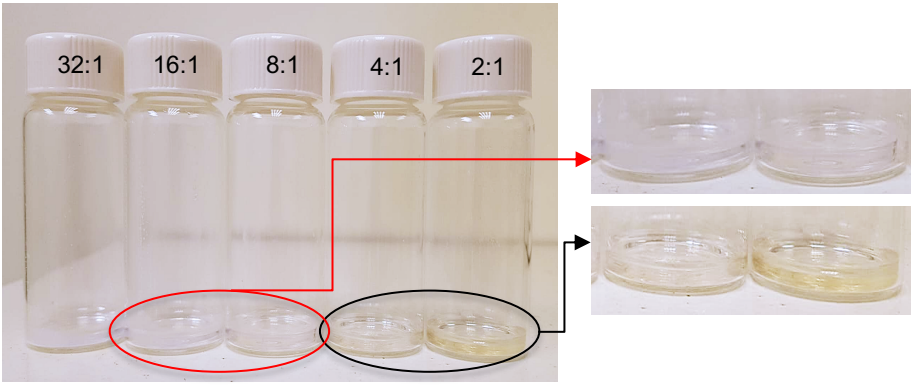

Figure 8. PSFs with different St:DVB proportions

However, independent of the ST:DVB ratio or the presence or not of DVB, the foils presented stability and all of them were glued to the bottom of the glass vial.

The PSfs were measured in the scintillation counter with the 25 µL of ^{99}Tc solution previously spread over the surface of the PSfs and evaporated to dryness to determine its detection efficiency and evaluate the quenching (SPQ(E)) present in each PSf. As Table 2 shows, the SQP(E) and the detection efficiency decreased as the concentration of DVB increased, excluding

the PSf with 1:0 proportion, which did not have crosslinker and appears in the middle of the series with no correlation with the rest of the samples.

Table 2. Detection values for PSfs with different St:DVB proportions

St:DVB	SQP(E)	Efficiency [%]
1:0	625 ± 12	38 ± 6
32:1	670 ± 10	57 ± 1
16:1	674 ± 5	54 ± 2
8:1	634 ± 5	49 ± 3
4:1	628 ± 7	41 ± 0,2
2:1	602 ± 7	37 ± 2

Regarding the stability of the measurements, they were acceptable with low dispersion of results. Along with the physical features of the PSfs vials, these results showed that the presence or not of DVB did not affect the stability of the foil and all the PSfs were attached to the vial. This fact made us think that the reason behind the change in the stability of the foil was the presence or not of porogen. In the next plot, the decrease in the efficiencies of detection can be seen as the concentration of DVB increased (Figure 9).

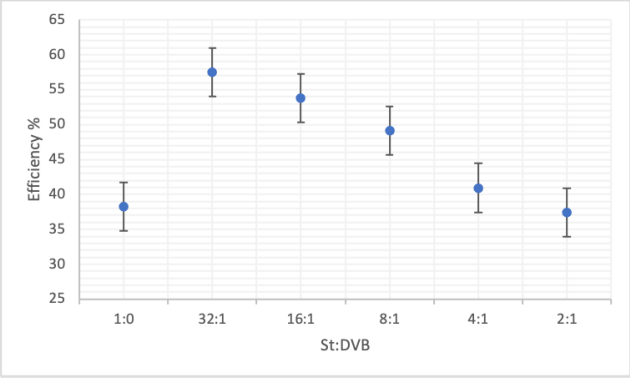

Figure 9. Efficiency of St:DVB series

Below is also shown the spectra of each one of the different St:DVB (Figure 10), and it can be seen that the spectrums are displaced to lower energies as the concentration of cross-linker increases.

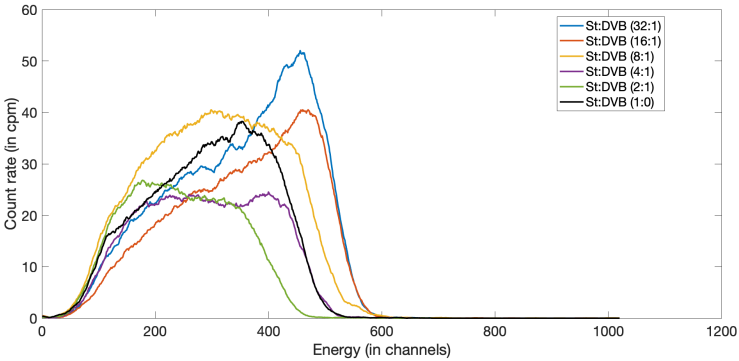

Figure 10. Overlapped spectra of PSFs with different St:DVB proportion

Three hypotheses can explain this behaviour. First, the opacity, especially present in 1:0, could interfere in the light transmission and transparency of the signal and cause optical quenching. Second, the colouration of PSfs when increasing the amount of DVB may have caused colour quenching and reduced the signal to lower SQP and efficiencies. In third term, decrease on detection efficiency can be caused due to chemical quenching by DVB since rigidity reduces energy transmission on the polymer chains.

6.1.3 PSfs prepared with purified monomers

In order to prove those hypotheses, another synthesis was made with 2:1 and 1:0 proportions (maximum and minimum amount of DVB) with a previous purification of DVB and St. This purification removed the inhibitor (4-tert-butylcatechol) present in both monomers, which may be causing the colouration along with other impurities. The new PSfs presented no colouration and the opacity of 1:0 disappeared (Figure 11).

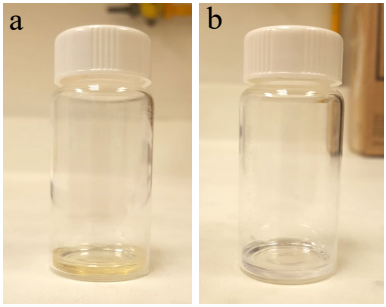

Figure 11. PSf 2:1 (a) Non-purified DVB (b) purified DVB

Once the results were obtained (Table 3), an improvement was seen in both SQP and the detection efficiency. It could be said that the colour quenching effects were reduced. This phenomenon not only had the benefit of obtaining higher SQP values and more energetic spectra. It also indicated that a higher concentration of purified DVB could be used, giving more resistance to the PSf without losing efficiency in the detection and reaching detection levels near 32:1 and 16:1 St:DVB values, which seemed to be the best ones with efficiencies above 50%.

Table 3. Detection values before and after purification of St and DVB

Vials	SQP	Efficiency [%]
1:0 non purified	625 ± 12	38 ± 6
1:0 purified	636 ± 14	54 ± 2
2:1 non purified	602 ± 7	37 ± 2
2:1 purified	653 ± 36	52 ± 4

Another conclusion was that the presence or not of cross-linker did not modify the scintillation parameters. Therefore, the possible chemical quenching modifying the transmission of light did not depend on the presence of DVB. Both types of PSfs (St-only and St:DVB) gave similar stable results in terms of efficiency with low dispersion. The comparison of each one of the spectrums before and after purification (Figure 12) are shown below.

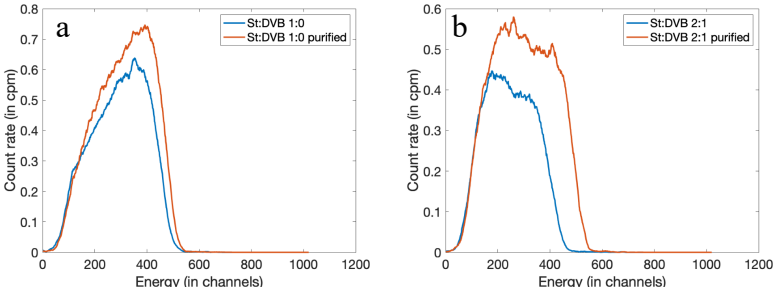

Figure 12. Spectra comparison of St:DVB series (a) 1:0 (b) 2:1

From these spectra it can be seen that in both cases, the PSfs with purified St and DVB were shifted to higher SQP values and presented more rigidity due to the cross-linker. Nevertheless, the shape of each one of them was different. The spectrum with the 1:0 proportion (a) presented more counts at high energy whereas the 2:1(b) had more counts in the low energy section of the spectrum. This could be related to the optical properties of the polymer, which could be affected by the presence of DVB.

Considering all the previous experiments regarding PSfs, it was concluded that there were two options for the synthesis of the PSkits. The first option would be the generation of PSkits without porogen due to fact that its presence reduced the stability of the foil. For this case, the best option considering detection efficiency would be the 32:1 St:DVB proportion.

On the other hand, keeping in mind the idea of the generation of pores in the PSf, the PSkits would count with the presence of a porogen and the highest concentration of DVB in order to give rigidity and chemical resistance. For this case, the best option would be 2:1 St:DVB proportion.

6.1.4 Optimum PSfs with heptane and toluene as porogens

Once the optimum PSfs were generated, porous 2:1 St:DVB PSfs were generated by adding porogen during the polymerization. Volumes of 0.25, 0.5 and 1mL of heptane or toluene were added to the polymerization solution.

PSf prepared with heptane showed a better capacity to be fixed to the vial than those prepared with toluene when they were rinsed with ethanol in the end-over-end mixer. In addition, heptane PSf presented white colour for volumes of 0.5 and 1 mL, which can be attributed to the presence of porous and the fact that the new material is non-homogeneous from the optical point of view. On the other hand, PSfs prepared with toluene seemed to reduce their adhesion to the vial as the concentration of porogen increased.

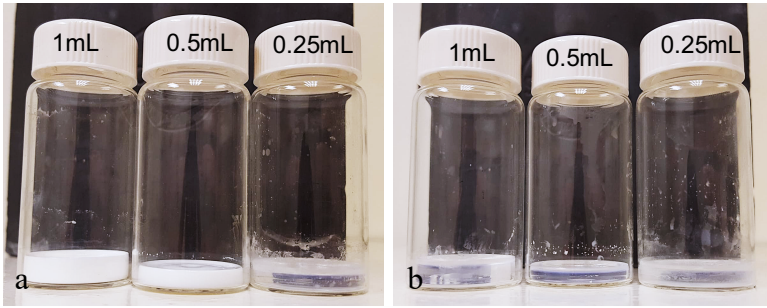

Figure 13. PSf in (a) heptane vials (b) toluene vials

As it can be seen in the previous Figure 13, heptane vials (a) showed an increase of volume as well as in white coloration of the PSf as the concentration increased. On the contrary, toluene vials (b) presented variations on their final volumes as the concentration the porogen increased. These variations made difficult the obtention of reproducible toluene PSfs and could affect the scintillation results. More experiments for toluene would be needed in order to ensure the reproducibility of the synthesis.

In order to see which of the PSfs presented irregularities or pores in the surface, they were observed with the scanning electron microscope (SEM). In the case of toluene PSfs, they presented rugosities in the surface of the foils and it could be seen little orifices similar to pores in the transversal section, as shown below.

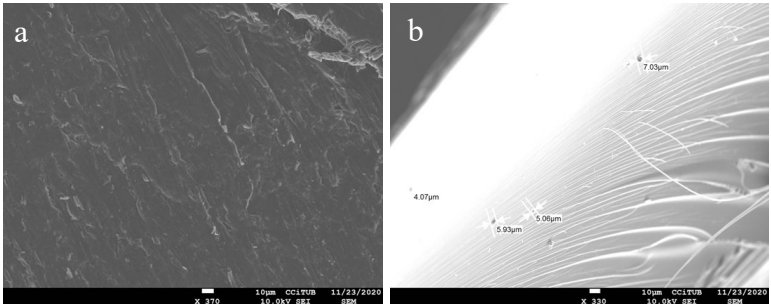

Figure 14. SEM images of PSfs with (a) toluene 1 mL (b) toluene 0.5 mL

Regarding the heptane PSf, they presented microspheres or rugosities in the surface of the PSf as well but, in the transversal section, a different texture appeared. It could not be classified as pores but there seemed to be conglomerations of polymer that may allow the diffusion of the sample.

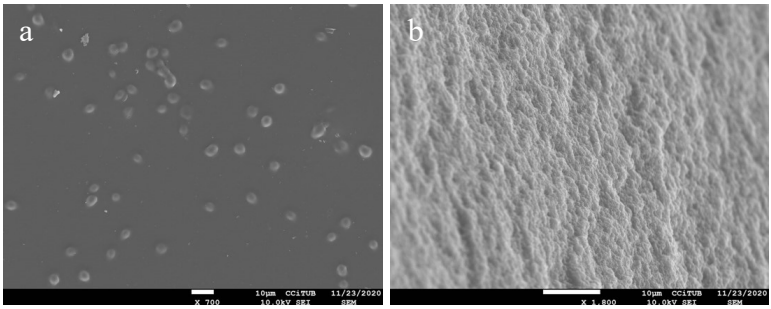

Figure 15. SEM images of PSfs with heptane (a) surface (b) transversal section

The PSfs with porogens were also measured by the scintillation counter after ^{99}Tc deposition and the results are shown below in Table 4.

For the toluene vials, the lack of reproducibility in the synthesis seemed to affect the scintillation measurement and the dispersion of results was higher than in the heptane ones. There was no clear correlation between the SQP values and the concentration of the porogen. However, the efficiencies of detection were around 35-47%, which would have been acceptable if there were no problems in the stability of the foils.

Table 4. Detection values for PSfs with toluene and heptane

Porogen amount	SQP	Efficiency [%]
Toluene 1 mL	760 ± 24	47 ±7
Toluene 0.5 mL	661 ± 23	35 ± 9
Toluene 0.25 mL	707 ± 7	43 ± 5
Heptane 1 mL	644 ± 5	52 ± 5
Heptane 0.5 mL	675 ± 41	49 ± 6
Heptane 0.25 mL	727 ± 14	45 ± 3

Regarding PSfs prepared with heptane, the efficiencies were higher than the toluene ones, with values around 45-52%. In this case, the correlation in the results was perfectly seen and as the concentration of heptane increased, the efficiency did it too, while the SQP decreased to lower energies.

This behaviour could be attributed to different opposed effects. The porosity could help to the introduction of the solution inside of the polymer structure which would increase the specific surface but, at the same time, porosity could make the transmission of light worse due to quenching. Lastly, with the increase of volume seen before in Figure 13, the PSf could be better positioned respect the PMT when the measurement was made and the efficiency increased.

Attending to the scintillation measurements, the SEM observations and the stability of the PSf, 1 mL of heptane as the porogen was selected to prepare the porous PSkits. Below is plotted the efficiency of each porogen series according the volume added (Figure 16).

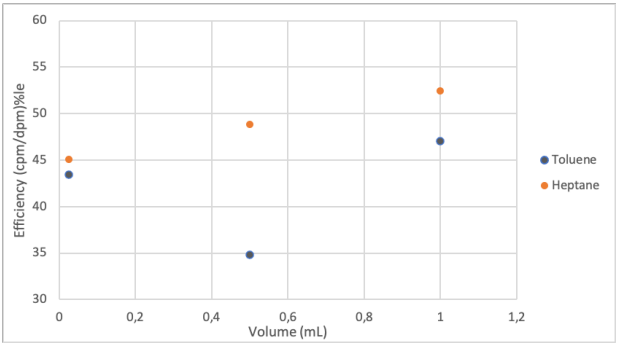

Figure 16. Efficiency vs Volume added

6.1.5 PSfs prepared in plastic vials

For the last PSfs experiment, a PSf in the St:DVB 2:1 proportion without porogen was synthesized in a plastic vial in order to compare the capabilities of glass and plastic PSkits. Once it was measured, a satisfactory detection efficiency of 82% was detected and the spectrum showed in Figure 17 below, was acceptable.

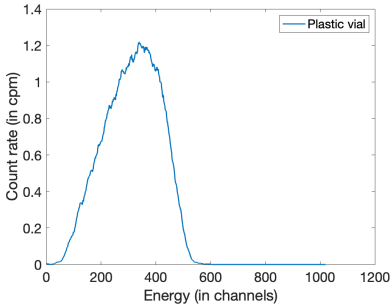

Figure 17. Spectrum of PSf in plastic vial without porogen

Certainly, both scintillation types of vials could be used for the study of ^{99}Tc.

6.2. PREPARATION OF THE PSKITS

For the preparation of a selective plastic scintillator for ^{99}Tc fast and simple analysis (PSkit), a solution of Aliquat 336® in methanol was poured over the surface of the PSf and after evaporation of the solvent in the oven, the extractant deposition on the PSf took place.

Two types of PSkits were prepared: 32:1 St:DVB proportion without porogen and 2:1 St:DVB proportion with 1 mL of heptane as porogen. PSktis were prepared in glass and plastic vials. The aim was to determine the best strategy to develop selective, stable and porous PSkits with the higher detection efficiency and retention values.

6.2.1. PSkits with 32:1 St:DVB proportion

The solution sample of ^{99}Tc was added to the PSkits and mixed manually. After more than 24h, the solution was removed from the PSkits and the scintillation measurement was made to see the ^{99}Tc retained. The removed solution was also measured to know the amount of ^{99}Tc non-retained and, therefore, be able to calculate the retention capacity of the PSkit. Below are shown the results of the measurement in Table 5.

Table 5. Comparison between glass and plastic scintillation vials 32:1

Vials	Efficiency[(a)] [%]	Retention [%]
Glass 32:1	20 ± 2	98.8 ± 0.2
Plastic 32:1	55 ± 2	97.9 ± 0.6

(a) Only technetium retained is measured

PSkits in both glass and plastic scintillation vials presented a good retention; almost quantitative for ^{99}Tc, but the plastic ones had higher efficiencies of detection. One of the reasons behind may lay in the structure of each type of vial, having the glass vial a plain surface which might difficult light transmissions whereas plastic vials presented a rugged surface that may allow better light transmission of photons thanks to diffuse reflection and transmission.

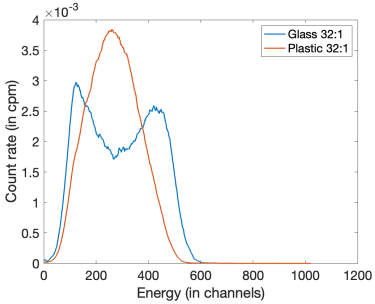

Figure 18. Spectra of retention in glass VS plastic

Looking at the spectra in Figure 18, it could be seen that the SQP values between them were slightly different as well as the shape of each spectrum. This behaviour may be related to the different positioning of the PSkits regarding the PMT along with the previous ones commented.

Obtaining efficiencies of 55% in plastic vials was extremely satisfactory because when working with plain PSkits, half of the particles emitted should not be detected. The only explanation of surpassing 50% of efficiency is that the PSkits in plastic presented some kind of porosity. In this particular case, no porogen was present in 32:1 plastic vials but they presented some irregularities that may have increased the specific surface and justified the high detection efficiency (Figure 19).

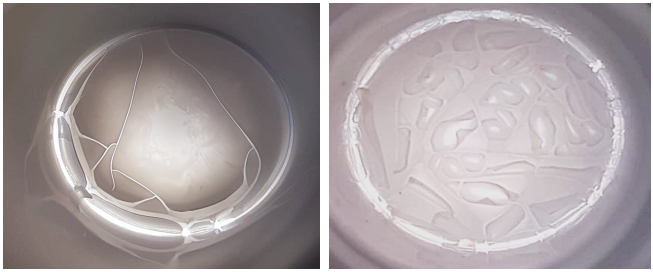

Figure 19. Top view of PSkits in plastic vials

6.2.2. PSkits with 2:1 St:DVB proportion and heptane as porogen

Following the same procedure as in the 32:1 St:DVB vials, the solution sample of ^{99}Tc was added to the PSkits, extracted after more than 24h and the scintillation measurement was made to see the ^{99}Tc retained. The removed solution was also measured, and the Table 6 below shows the results of the measurement.

Table 6. Comparison between glass and plastic scintillation vials 2:1

Vials	Efficiency[(a)] [%]	Retention [%]
Glass 2:1	0.03 ± 0,09	16 ± 15
Plastic 2:1	65 ± 3	96.7 ± 0.9

(a) Only technetium retained is measured

On this study, the PSkits in the glass vials were not properly linked to the bottom of the vial (Figure 20). In addition, there was no retention of ^{99}Tc and almost all the disintegrations registered appeared in the removed solution from the PSkits. This phenomenon proved that the lack of stability when dealing with PSkit with porogens in glass vials can cause an inefficient retention of the radionuclide.

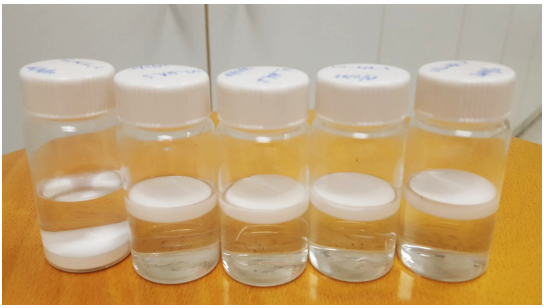

Figure 20. PSkits 2:1 with heptane in glass vials

Regarding the plastic ones, they seemed to be the most suited for scintillation measurement, obtaining efficiencies of 65%. The presence of porous helped to increase the detection above 50% and the retention for technetium was of 97%.

In the next plotting (Figure 21), plastic vials with 32:1 and 2:1 St:DVB are compared. It can be seen that both spectra are similar in energy (SQP) and in shape. So, it can be said that scintillation plastic vials gave better results than the glass ones in terms of efficiency detection and retention for ^{99}Tc.

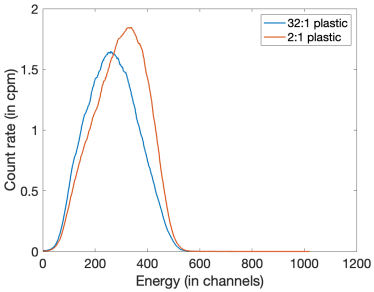

Figure 21. Retention spectra comparison between 32:1 and 2:1 plastic vials

6.2.3. Time of exposure

The last experiment was performed to obtain information about the influence of the time of contact between the solution and the PSkits in the extraction of the radionuclide. The PSkits used were the 32:1 proportion without porogen in glass vials.

Table 7. Time exposure efficiencies

Time of exposure	Efficiency 2[(a)] [%]	Retention [%]
24 h	20 ± 2	98.8 ± 0.2
10 min	13 ± 2	85 ± 3

(a) Only technetium retained is measured

As shown in Table 7, the detection efficiency in glass vials after 24h hours was 20% and the retention of technetium was remarkably high. Regarding the vial with 10 minutes of solution-PSkit exposure, the detection efficiency lowered until 13%, but the retention was still high, with values around 85%.

From this comparison, it can be concluded that good retention values can be maintained with lower times of exposure. However, this reduction in time may affect the efficiency of detection, which experimented an important decrease. In order to optimise the time of exposure and ensure that the detection efficiency given is satisfactory, further experimentation and study are required.

7. CONCLUSIONS

In summary, stable PSfs have been synthesized by polymerization technique with the presence or not of porogen and, with the addition of the extractant, the final PSkits have been obtained.

It has been proved that the purification of the monomers St and DVB is required in order to avoid colour quenching and opacity. Moreover, the presence of DVB does help with giving rigidity and chemical resistance to the PSkit without modifying the detection efficiency. However, the spectra can experiment a decrease in SQP as the concentration of DVB increases.

All the PSkits presented selectivity for ^{99}Tc with detection efficiencies of 20% for glass scintillation vials and over 55% for the plastic ones.

Nevertheless, there was a lack of reproducibility in the synthesis of PSkits in glass vials with porogen, especially when toluene was used due to the fact that toluene's behaviour during the synthesis complicated the obtention of stable PSkits.

The synthesis of the PSkits was stable for plastic scintillation vials when heptane was used as the porogen or when the synthesis was carried out in glass vials without porogen.

The radioactivity and retention measurements in the stable PSkits had low dispersion of results and they were reproducible. With retention values for ^{99}Tc around 97-98% for plastic and glass vials respectively, it can be concluded that this first approach to the application of these PSkits in aqueous samples has resulted satisfactory.

Lastly, it has been found that the extraction of the radionuclide has dependence with the time of exposure of the PSkit with the samples. Proper optimization will be needed to improve the future application on-field.

On the whole, this study has become a promising step towards the obtention of a more economic and fast-selective screening method for beta emitters like technetium.

8. REFERENCES AND NOTES

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9. ACRONYMS

AIBN	2,2'-Azobis(2-methylpropionitrile)
CPM	Counts per minute
DVB	Divinylbenzene
LS	Liquid scintillation
LSC	Liquid scintillation cocktail
NPP	Nuclear Power Plant
PMT	Photomultiplier
POPOP	1,4-bis(5-phenyl-2-oxazolyl) benzene
PPO	2,5-Diphenyloxazole
PS	Plastic scintillation
PSm	Plastic scintillation microsphere
PSf	Plastic scintillation foil
PSkits	Plastic scintillation kits
PSr	Plastic scintillation resin
SEM	Scanning electron microscope
SQP(E)	Standard Quenching Parameter (external)
St	Styrene